Superconductivity in carbon nanotubes coupled to transition metal atoms.

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The electronic structures of zig-zag and arm-chair single-walled carbon nanotubes interacting with a transitional-metal atomic nanowire of Ni have been determined. The Ni nanowire creates a large electron density of states (DOS) at the Fermi energy. The dependence of the enhanced DOS on the spin state and positioning of the transition-metal wire (inside or outside the nanotube) is studied. Preliminary estimates of the electron-phonon interaction suggest that such systems may have a superconducting transition temperature of $\sim$ 10-50 K. The signs of superconductivity seen in "ropes" of nanotubes may also be related to the effect of intrinsic transition-metal impurities.

The discovery of carbon nanotubes (CNT) has given rise to fascinating basic physics as well as tantalizing technological possibilities[1]. The synthesis of CNTs naturally incorporates transition-metal (TM) atoms like Ni, Co, which are used as "seeds" for initiating growth. In addition, TM impurities are found in CNTs, as adsorbed species inside or outside the CNT walls. TM atoms occurring as substitutional impurities are energetically unfavourable, and annealing converts them into adsorbed species[2]. Many studies of CNTs with alkali, Au, Ti, Co, Ni, etc., and rare earth atoms, have appeared in the literature and have clarified the binding energies and other aspects of these systems[1, 3]. Given the strong $d-d$ interaction of TM atoms, and the directionality imposed by the CNTs, the TM atoms may form quasi one-dimensional transition-metal nano-wires (TMWs), on the inner or outer surface of the CNTs[4]. From a theoretical point of view, the 1-D structure of the CNT, and the 1-D TMW, provide a realization of Luttinger liquids, Bethe ansatz problems, and novel spintronics.

The TMW transfers electrons to the CNTs and can transform semi-conducting CNTs into metals. If the electron density of states (DOS) at the Fermi surface could be strongly enhanced, the coupled system may respond by undergoing a Peierls or a Cooper-pairing transition. In fact, the possibility of superconductive interactions in pure CNTs themselves has been discussed, mainly within the Luttinger-liquid paradigm[5]. Evidence for superconducting fluctuations, proximity effects etc., in CNTs have been reported [6]. The quasi 1-D nature of the TM chain, and the CNT are modified by coupling them when electrons can hop from the CNT to the TMW and back. The Cooper pairing would involve electronic and phononic effects associated with the Ni-C as well as the Ni-Ni and C-C interactions. Even if these do not lead to superconductivity, we may expect some interesting and technologically exploitable properties from the TMW/CNT system.

The objective of this paper is to use tight-binding (TB) schemes, supported by density-functional first-principles calculations, for calculating the electronic energy bands, the density of states, and phonon properties of CNTs coupled to TMWs. The TB results are used for a preliminary discussion of the possibility of superconductivity in these systems. It is concluded that coupled CNT/TMW systems are promising superconductive materials whose special properties may be valuable in a variety of novel applications.

We use TB parameters obtained from fitting to first-principles calculations, or by adapting from Harrison's universal parameters[7] when justifiable. Our simulation cells (SC) contain one or two TM atoms and also one or two CNT unit cells, as the case may be. Single-walled CNTs are specified by the pair of numbers (n,m) which defines the chirality of the nanotube. These numbers specify the way a 2-dimensional graphite sheet is rolled to obtain the CNT. While the π- electron system in the generic graphite sheet makes it conducting, the metallic or semiconducting nature of the CNT (i.e, its bandgap) is determined by the chosen (n,m) configuration. In this study we consider the two extreme sets, (n,0) and (n,n), which correspond to the zig-zag (ZZ) and arm-chair (AC) configurations.

The use of two Ni atoms per simulation cell allow us to consider ferro- or antiferromagnetic nearest-neighbour coupling. If one TM atom per SC were used, the Ni-Ni interaction is negligible and we have the case of doping with almost isolated TM atoms. A first-principles study of a 1-D chain of Ni atoms in isolation has been carried out by Freeman and colleagues[8], and used to obtain the tight-binding parameters for the Slater-Koster method. While the diagonal parameters are strongly modified from the "universal" parameters of Harrison, the off-diagonal universal parameters are quite close to the results obtained from the fit to the first-principles calculations. The TB parameters are further evolved into a set of parameters which depends on the antiferromagnetic or ferromagnetic coupling between Ni neighbours by making the on-site energy of the Nickel d-orbital a function of the spin state of the Ni atom. Thus we have used $\epsilon_d \uparrow - \epsilon_d \downarrow = J$ with

a value of J corresponding to the bulk Ni value. A better estimate, suitable for the 1-D chain may be obtained by fitting to a first-principles calculation, but the results are found to be rather insensitive to the spin configuration and may be considered illustrative. The bandstructure and DOS of the Ni wire (uncoupled from the CNT) are seen in panel (a) of Fig. 1. Here the, Ni wire which registers with the armchair CNT is a linear chain. The Ni wire which registers with the zigzag CNT is itself a zigzag chain. Its bandstructure and DOS before coupling to the CNT are shown in panels (a) of Fig. 2.

In panels (b) of Figs. 1, 2 we show the bandstructure and DOS of the CNTs before coupling to the TMWs. The Slater-Koster approach for obtaining the electronic states of CNTs within a sp^3 basis is used. Many TB calculations for CNTs have been reported and the procedure is now well established. The AC(9,9) CNT, panel (b) of Fig. 1, has two bands crossing the Fermi energy near 2/3 of the $\Gamma - X$ line and hence it is metallic. The ZZ systems become metallic for specific values of n (for multiples of 3), and the bandgap for the semiconducting case is, to first order, a function of $1/d$. Here d is the ideal CNT diameter given by $d = (a_L/\pi)(m^2 + m^2 + mn)^{1/2}$, where $a_L = 0.245$ nm is the lattice constant in the 2-D graphene sheet. Panel (b) shows a very small flat DOS at E_F for the isolated CNT. Figure 2 shows, in panels (b) the bandstructure and DOS of the zig-zag (12,0) nanotube without coupling to the TMW. Here also, although the nanotube is metallic, its small DOS at E_F is hardly visible in panel (b).

We position the nanowire inside, or outside the CNT, and interacting with the carbon s and p bonded network forming the CNT wall. The TMW binds chemically to the CNT, unlike in the case of, e.g., Au or Al. The interaction of Ni atoms with CNTs have also been studied by Andriotis et al.[2], who determined the relaxation of substitutional and also adsorbed Ni atoms near (or inside)a single-walled CNT. Their simulations show that a Ni atom may migrate into a CNT, from the outside, using a vacancy in the CNT wall. These calculations, as well as other studies, already provide us with information regarding the optimal Ni-C distance (~ 0.2 nm). For the two-Ni SC we have taken the Ni-Ni bond to be nearly the same as that of the isolated nanowire[8], and registering with the a_L distance on the CNT wall. This is consistent with the fact that the local structure of the CNT is only minimally affected by the presence of an adsorbed Ni atom inside or outside the CNT wall. However, as seen from our calculations, a large electron density of states is created at the Fermi point by the Ni nanowire, and the CNT becomes conducting, even if it were originally semiconducting (however, this is not always the case in Ti nanowires). The results for the coupled CNT/TMW are given in panels (c) of Figs.1-2.

The bandstructure of the Ni-wire/CNT system, panel (c), shows a nearly dispersionless ("flat") band which
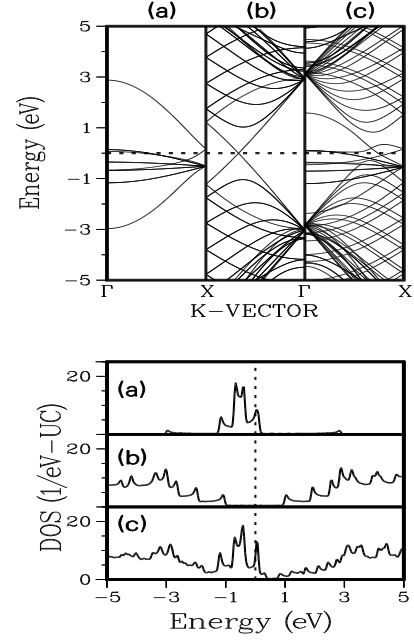

FIG. 1: Energybands and DOS of (a) chain of ferro-magentic Ni atoms, (b) arm-chair CNT (9,9) and (c) the coupled system Ni-wire/CNT with the TMW adsorbed on the outside wall. The DOS is per eV per simulation cell (SC) with 72 carbon atoms and 2 Ni atoms.
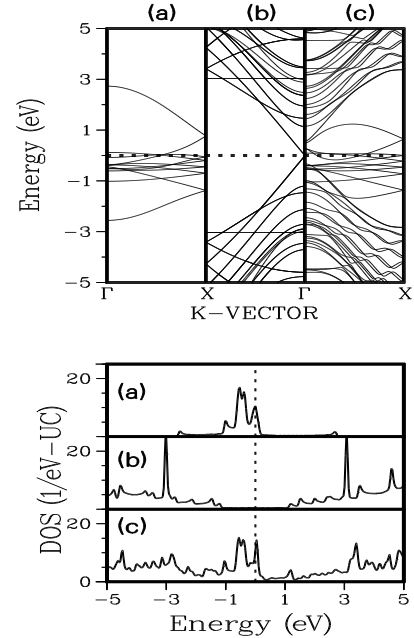

FIG. 2: Energybands and DOS of (a) chain of ferro-magentic Ni atoms, (b) zig-zag CNT (12,0) and (c) the coupled system Ni-wire/CNT with the TMW adsorbed on the outside wall. The DOS is per eV per simulation cell (SC) with 48 Carbon atoms and 2 Ni atoms.

crosses the Fermi energy, and also other Ni-like bands which show greater dispersion. The "flat" band relates to electron hopping via the Ni-C bond which is localized. It provides transport via hopping from the CNT to the TMW and back. The bands with linear dispersion found at the Fermi energy of isolated AC nanotubes (used in bosonization approaches) are no longer present in the coupled CNT/TMW systems. Note that the linear-k bands crossing E_F in panel (b) have been repelled apart in the coupled AC system (c) and the bands derived from the Ni atoms are inserted near the Fermi energy. Also, the doubly degenerate bands in panel (b) are split in panel (c).

The density of states of the Ni chain, the (9,9)CNT and the coupled system are shown in Fig. 1. The main change in the DOS is the enhancement at and around the Fermi energy. The splitting of the bands has smoothened the DOS, as seen by comparing panels (b) and (c). Similar results are found in the density-functional calculations of Yang et al for metallic Ti nanowires coupled to CNTs.

Our calculations, and those of Yang[4] for Ti show that there is significant electron transfer between the CNT and the TM. The density of states $N(\epsilon_F)$ for one-Ni atom in the simulation cell (i.e, isolated Ni atoms) is three to four times stronger than the case with two-Ni atoms per cell. The TM wire retains some of its electrons on the wire, while the isolated Ni atoms inject more electrons into the CNT (this needs further confirmation from a more microscopic calculation). On the other hand, if one Ni atom were used in a simulation cell of 3 units, then the doping level would be lower and the effect is less. This implies that about 3-4% of Ni atoms in (9,9) or (12,0) nanotubes would be optimal for a highly enhanced $N(\epsilon_F)$.

The presence of a significant density of states at the Fermi energy opens the possibility of structural relaxation via the electron-lattice interaction. This was in fact considered by Mintmire et al., and also Saito et al.[9], who concluded that the CNTs are stable with respect to Peierls-type distortions. The density-functional total-energy minimisations of Yang et al.[4] for CNTs coupled to Ti nanowires show only a slight local modification of the CNT lattice. Our calculations agree with this and the main effect arises from electron transfer and self-consistent readjustment of the Fermi energy. Hence we conclude that, even if isolated CNTs are unstable, the coupled CNT/TMW systems are stable with respect to Peierls distortions, and that the enhanced DOS, $N(\epsilon_F)$ at the Fermi energy is available for modification by more subtle processes like Cooper pairing.

Graphite intercalation compounds (GIC) have very low transition temperatures $T_c \sim 1$ K, and $N(\epsilon_F)$ values of $\sim$ 1-2 states/eV-spin for 60 Carbon atoms, and compares with the $N(\epsilon_F) \sim 10$ states/eV-spin-C_{60} of alkali-doped fullerenes (ADF). Superconductivity in the ADFs have been discussed using purely electronic mechanisms[10],

but mostly using the McMillan-Eliashberg (ME) approach within the Migdal approximation[11]. Migdal's approximation is more easily justified in the CNT/TMW systems for processes mediated by the heavy transition-metal atoms. Schluter et al.[11], argued that the electron-phonon interaction in the ADFs is larger than in GICs because of the curvature effect absent in the GICs[11]. This argument applies equally to CNTs. The superconductivity in ADFs involves not only the "on-ball" processes, but also the much weaker hopping in a 3-D system of fullerene molecules. In studies on superconductivity of CNTs, the quasi 1-D character is claimed to be overcome by weak hopping between single CNTs in "ropes" of nanotubes. This hoping involves tunnelling through non-bonding interactions and is very poor. In fact, calculations by Delaney et al.[12] show that the non-bonding interactions suppress the 1-D conductivity. On the other hand, in CNT/TMW coupled systems, electron transfer between two nanotubes occurs effectively via physical metallic contact between TMWs on adjacent CNT/TMW strands. Hence the systems aquire 3-D character and the main issue is to study the nature of the interactions on the individual CNT/TMW elements.

A force-constants model for the CNTs[13], extended to include Ni-Ni and Ni-C interactions can be used to study the phonons of the CNT/TMW system. Depending on the force constants we use, the high frequency Ni-Ni vibrations fall between 200-300 cm^{-1} and strongly interact with the "breathing" and "twisting" modes of the CNTs, while leaving the carbon high-energy optical modes relatively unaffected, except for lifting all degeneracies. The axial symmetry of the isolated CNT is broken in the coupled system, and a rich redistribution of the low-energy phonon modes is found.[14] The radial modes are not too important in ADFs since they have little effect on the electronic structure at the Fermi level. In contrast, radial modes in the CNT/TMW systems couple strongly with the Fermi level bandstructure, and are many times more efficient in electron-phonon (e-p) coupling than the stiffer tangential modes. The e-p interaction associated with electron hopping between the CNT and the TMW, and along the TMW would bring new, strong coupling features absent in the pure CNTs. Electron transport in the Ni bands would also be subject to strong e-p interactions. The electron-phonon coupling constant is of the form

$$\lambda = N(\epsilon_F)V = N(\epsilon_F)\sum_i \eta_i / <M_i\omega_i> \qquad (1)$$

where the sum runs over all vibrational modes, with atomic masses M_i, and ω_i and η_i being averaged contributions from phonon frequencies and Hopfield factors for the electronic states. The $N(E_F)$ depends somewhat on the Ni-spin configuration (ferro or antiferro), the location of the TMW (inside or outside the CNT), and the nature of the CNT (ZZ, AC), as seen in Table I, but a

TABLE I: electron density of states per eV per spin per electron in CNT/TM coupled systems. With two Ni atoms in the simulation cell, Ferromagnetic (F) and antiferromagnetic (AF) alignments are given. With one Ni atom/simulation cell, there are no Ni-Ni interactions.

system	(12,0)	(13,0)	(9,9)
F Ni_2 in	0.03	0.035	0.015
AF Ni_2 in	0.04	0.03	0.02
F Ni_2 out	0.035	0.03	0.015
AF Ni_2 out	0.036	0.033	0.019
Ni_1 out	0.08	0.08	0.06

"grosso modo" value is 0.035 states/(eV-spinstate). To clarify the notation we have used here, $(12,0)FNi_2$ indicates a calculation for a ZZ nanotube with two Ni atoms in a simulation cell containing 1 unit cell of the ZZ-CNT. Hence there are 48 carbon atoms, with 192 states, and each Ni atom has one s and 5 d states. The total number of spin-states is 408 per simulation cell, yielding a total $N(\epsilon_F)$ of about 12 states per eV per simulation cell. The number reported in the Table is the $N(\epsilon_F)$ per eV per spin-state. In the (9,9)AC system we use one unit cell in the simulation cell, giving 72 carbon atoms and two Ni atoms. The normalization enables us to compare the different structures given in Table I. When there is only one Ni atom per SC, there are no Ni-Ni interactions and the Ni electrons are (3-4% doping) most effective in augmenting the $N(\epsilon_F)$ in ZZ nanotubes.

The 0.035 per eV per spin-state as defined previously is comparable to that in ADFs where $N(E_F)$ of 2-8 states/(eV-spin-C_{60}) have been quoted[11, 15] The T_c depends on the Coulomb parameter $\mu*$. Koch et al.[16] have argued that $\mu*$ is $\sim$ 0.1-0.2 even though the reduction due to retardation effects is absent in fullerene-like systems. Hence, using this range of parameters, the T_c of CNT/Ni-wire coupled systems is found to be in the range 10-50 Kelvin.

A natural implication of our study is that the observed signs of CNT superconductivity[6], e.g., in "ropes" of CNTs may be due to intrinsic doping by TM impurities which cannot be removed completely[17]. This can be examined via experiments in which the TM impurities are added or leached out in a controlled way. When isolated Ni atoms are attached, e.g, one Ni per 48 carbon atoms in a (12,0) CNT, the $N(\epsilon_F)$ is enhanced. The random Ni-Ni contacts between such CNTs in ropes of CNTs could provide the higher dimensionality needed to stabilize the superconductivity. In conclusion, our calculations on CNT/TM systems suggest that couplings to suitable TM atoms stabilize any inherent superconductivity in the CNTs. These conclusions, based on tight-binding methods should stimulate more microscopic calculations as well as new experiments.

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